

## Mapping a Homopolymer onto a Model Fluid

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### Abstract

We describe a linear homopolymer using a Grand Canonical ensemble formalism, a statistical representation that is very convenient for formal manipulations. We investigate the properties of a system where only next neighbor interactions and an external, confining, field are present, and then show how a general pair interaction can be introduced perturbatively, making use of a Mayer expansion. Through a diagrammatic analysis, we shall show how constitutive equations derived for the polymeric system are equivalent to the Ornstein-Zernike and P.Y. equations for a simple fluid, and find the implications of such a mapping for the simple situation of Van der Waals mean field model for the fluid.

**Keywords:** linear molecules, simple fluid, graphical analysis

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# 1 Introduction

Molecules with linear chains as descriptive backbones can, in whole or in part, be constructed by temporally ordered sequences of additions. The efficiency of such a process recommends chains as major actors in molecular biology, as well as in industrial chemistry. They may be examined at multiple levels of resolution. In the study about to be reported, a very coarse description is used in which the units are taken as point entities with next neighbor strong binding forces and weak non-next neighbor interactions, all in the presence of a confining external field. Even more narrowly, we restrict our attention to homopolymers, but will indicate how questions concerning the statistics of heteropolymers can be addressed within this format.

In further detail, we study a single homopolymer in classical thermal equilibrium. The homopolymer context suggests, in analogy with fluids, extension to a bath of monomers which can join or leave the chain, inducing fluctuations in the monomer number  $N$  and creating what might be termed a monomer grand ensemble. The corresponding formalism also follows the fluid model: suppose there are  $N'$  monomers in the full system,  $N$  of which are bound together to create a polymer,  $N' - N$  being free in the volume  $V$  envisioned. Then the canonical partition function of the complete system takes the form (one needs at least  $N = 1$  to declare a polymer)

$$Q_{N',V}^{TOT} = \sum_{N \geq 1} \frac{(VQ^{(m)})^{N'-N}}{(N'-N)!} Q_N^{(p)}(u) \quad (1)$$

where  $Q^{(m)}$  is the monomer canonical partition function in its center-of-mass coordinate system,  $Q^{(p)}$  that of the  $N$ -monomer polymer in the external potential field  $u$ . The “grand” partition function of the monomer collection defining the polymer will then be taken as

$$\Xi^{(p)}(\zeta) = \lim_{N',V \rightarrow \infty} \frac{N'!}{(VQ^{(m)})^{N'}} Q_{N',V}^{TOT} \quad (2)$$

or via the Stirling approximation,

$$\begin{aligned} \Xi^{(p)}(\zeta) &= \lim_{N',N \rightarrow \infty} \sum_{N \geq 1} \left( \frac{N'/V}{Q^{(m)}} \right)^N Q_N^{(p)}(u) \\ &= \sum_{N \geq 1} \zeta_0^N Q_N^{(p)}(u), \quad \zeta_0 = \frac{(N'/V)}{Q^{(m)}}, \end{aligned} \quad (3)$$

identifying the fugacity as

$$\zeta(r) = \zeta_0 e^{-\beta u(r)} = e^{\beta \mu(r)}. \quad (4)$$

The expression (3) is very convenient for formal manipulations, but a certain amount of caution must be exercised. In particular, number fluctuations can be very large, as we will see, so that “canonical” - i.e. fixed monomer number - information, requires care.

In this paper, our aim is to show how (3) allows for a familiar type of diagrammatic representation, which not only gives rise to a systematic perturbation expansion in the strength of the non-next neighbor forces, but also - under special but physically reasonable restrictions - maps onto a suitable classical fluid, with its array of well-tested computational recipes. With this, we can routinely examine the effect of structured fields on the polymer density profile, which is our implicit objective.

## 2 The Reference System [1]

Now let us introduce explicit notation following [2]. The model homopolymer that we will deal with has as monomer units point “particles” located at  $\{r_i, i = 1, \dots, N\}$ , which may be imagined as spatial locations, but can include type, internal state, etc. There is an external potential field  $u(r)$  appearing only in the combination  $\zeta(r) = \zeta_0 e^{-\beta u(r)}$ , where  $\beta$  is the reciprocal temperature, and a next neighbor potential  $\phi(r, r')$ , typically  $\phi(r - r')$ , with associated Boltzmann factor  $w(r, r') = e^{-\beta \phi(r, r')}$  as well as a general pair interaction (including next neighbors)  $v(r, r')$ , giving rise to the Mayer function  $f(r, r') = e^{-\beta v(r, r')} - 1$ . Note that we can expect that  $w \rightarrow 0, f \rightarrow 0$  as  $|r - r'| \rightarrow \infty$ . When  $r$  represents real space location alone, we have the format of freely jointed units, but that is not intrinsic, since the units can involve more than one monomer (see e.g. [3]).

We will choose, as generating function for the thermodynamics, the grand canonical potential

$$\Omega[\zeta] = -(1/\beta) \ln \Xi^{(p)}[\zeta], \quad (5)$$

so that, e.g. the resulting monomer density profile will be given by

$$\begin{aligned} n(r) &= -\zeta(r) \frac{\delta \beta \Omega[\zeta]}{\delta \zeta(r)} \\ &= + \frac{\delta \ln \Xi^{(p)}[\zeta]}{\delta \ln \zeta(r)} \end{aligned} \quad (6)$$

To start with, consider the “reference system” in which the general pair interactions have not yet been included. Since the monomers can be labeled ordinally along the chain, and they are not equivalent with respect to system energy, there is no statistical weight factor for an  $N$ -monomer configuration. Hence (3) can be written as

$$\begin{aligned}
\Xi^{(p)}[\zeta] &= \zeta_0 \int e^{-\beta u(r_1)} dr_1 + \zeta_0^2 \int \int e^{-\beta u(r_1)} w(r_1, r_2) e^{-\beta u(r_2)} dr_1 dr_2 + \\
&\quad + \zeta_0^3 \int \int \int e^{-\beta u(r_1)} w(r_1, r_2) e^{-\beta u(r_2)} w(r_2, r_3) e^{-\beta u(r_3)} dr_1 dr_2 dr_3 + \dots \\
&= \int \zeta(r) dr + \int \int \zeta w \zeta(r, r') + \zeta w \zeta w \zeta(r, r') + \dots dr dr' \\
&= \langle 1 | \zeta (I - w \zeta)^{-1} | 1 \rangle
\end{aligned} \tag{7}$$

where  $w$  is regarded as a (continuous as needed) matrix,  $\zeta$  a diagonal matrix,  $I$  ( $I(r, r') = \delta(r, r')$ ) the identity, and  $1$  the vector of all 1's. The validity of (7) is subject to convergence. In terms of the molecular weight control parameter  $\zeta_0$ , it is apparent that (7) will converge only until  $\zeta_0 \text{ MAX} = 1/l_{\text{MAX}}(w e^{-\beta u})$  - the value at which the minimum eigenvalue of  $w \zeta$  reaches 1. The behavior of the system as  $\zeta_0 \rightarrow \zeta_0 \text{ MAX}$  must be factored out. Combining (6) and (7), we have, using the standard  $(A^{-1})' = -A^{-1} A' A^{-1}$  for any derivative ( $'$ ) on any matrix inverse, the mean density profile

$$n(r) = \frac{\langle 1 | \zeta (I - \zeta w)^{-1} | r \rangle \zeta(r) \langle r | (I - w \zeta)^{-1} | 1 \rangle}{\Xi^{(p)}[\zeta]} \tag{8}$$

In particular, the mean number of monomers,  $\overline{N} = \int n(r) dr$ , becomes

$$\overline{N} = \frac{\langle 1 | \zeta (I - w \zeta)^{-2} | 1 \rangle}{\langle 1 | \zeta (I - w \zeta)^{-1} | 1 \rangle} \tag{9}$$

dominated by  $\overline{N} = \zeta_0 \text{ MAX} / (\zeta_0 \text{ MAX} - \zeta_0)$  as  $\zeta_0 \rightarrow \zeta_0 \text{ MAX}$ . Thus, large mean molecular weight occurs very close to the “resonance” at  $\zeta = \zeta_0 \text{ MAX}$ . The effect is brought out forcefully by computing the standard deviation of  $N$  in a similar fashion:

$$\delta N = \left( \zeta_0 \frac{\delta \overline{N}}{\delta \zeta_0} \right)^{1/2} \sim \overline{N}, \tag{10}$$

evidence of something like an exponential distribution.

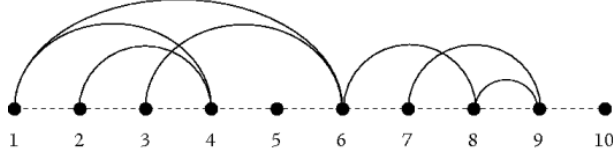


Figure 1: Example of diagram in expansion (11).

It is also useful to look ahead and see how the qualitative behavior will be modified in the presence of non-next neighbor interactions, which of course contribute  $N^2$  terms to the configurational energy. If all  $N^2$  were positive and of similar magnitude (e.g. long-range) they would append a convergence factor of the form  $e^{-\alpha N^2}$  to the series (7). This strategy is being investigated. However the non-next neighbor forces of physical interest are not necessarily long-range, and have a substantial attractive component. If the monomers are prevented from clustering, their forces would again contribute to the order of  $N$ , and would simply modify the reference system pathology. Short range forces would reinforce this prohibition, but in the model we will attend to, it is mainly the profile shaping due to the confined external potential that is relied on.

### 3 Diagrammatic Analysis

We proceed to the fully interacting homopolymer ensemble. In terms of  $e^{-\beta v(r, r')} = 1 + f(r, r')$ , the  $N^{th}$  term in (7) becomes

$$\int \dots \int \Pi'_{i,j} (1 + f(r_i, r_j)) \zeta(r_1) w(r_1, r_2) \zeta(r_2) w(r_2, r_3) \dots w(r_{N-1}, r_N) dr_1 \dots dr_N, \quad (11)$$

where  $\Pi'$  is the product over  $\frac{1}{2}N(N-1)$  distinct unordered pairs; thus a typical term of the full expansion, in terms of multinomials on  $f$ , would be diagrammatically like the one shown in Fig.11, with multiplicative Boltz-

mann factor represented by:

$$\begin{aligned}
\bullet &= \zeta(r) && \text{external field} \\
r \text{ --- } r' &= w(r, r') && \text{next neighbor weight} \\
\text{r} \text{ --- } \text{r}' &= f(r, r') && \text{general pair Mayer factor}
\end{aligned} \tag{12}$$

All field points  $r_i$  are integrated over. It will be convenient to introduce the matrix:  $\bigcirc \text{-----} \bigcirc$  denoted by  $\Lambda$ , for  $N \geq 2$ , in which the endpoints have weight 1 and are not integrated over, but the sum of all diagrams over all  $N \geq 2$  is included. Hence

$$\Xi^{(p)}[\zeta] = \langle 1 | \zeta \rangle + \langle \zeta | \Lambda | \zeta \rangle \tag{13}$$

where the vector  $|\zeta\rangle = \zeta|1\rangle$ .

Now various diagram reductions can be carried out. The basic one stems from the observation that some of the vertices are articulation points in the sense that their removal disconnects the diagram into a left and right half, e.g.  $r_6$  and  $r_9$  in Fig.1.

The end points are never given the status of articulation points. If the matrix belonging to the sum of all connected diagrams - those with no articulation points, those with endpoints ( $\bigcirc$ ) unintegrated, is denoted by  $C$ , then clearly  $\Lambda = C + C \zeta C + C \zeta C \zeta C + \dots$ , or:

$$\Lambda = (I - C \zeta)^{-1} C, \tag{14}$$

and (13) can be written as

$$\Xi^{(p)}[\zeta] = \langle 1 | \zeta ((I - C \zeta)^{-1} | 1 \rangle. \tag{15}$$

Of course, in the absence of the general pair interaction,  $C = w$ , and (15) reduces to (7).

But  $C$  can also be built up from  $\Lambda$ . To do this, observe that  $C$  consists of two types of diagrams,  $C_1$ , in which the endpoints have a direct f-link to each other, and  $C_0$  in which they don't. See Fig.2 for examples. Since the end-linked diagrams  $\Lambda_1$  of  $\Lambda$  are precisely the end-linked diagrams of  $C_1$  of  $C$ , and since  $C_1 = f * (\Lambda - \Lambda_1)$  we have

$$C_1 = f * (\Lambda - C_1), \tag{16}$$

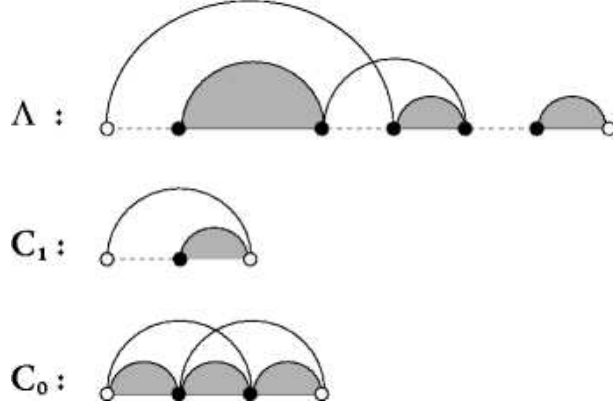


Figure 2: Examples of graphs included in  $\Lambda, C_1$ , and  $C_0$ . The shaded gray areas indicate the presence of any possible subgraph.

where  $A * B$  denotes element by element multiplication of the matrices  $A$  and  $B$ . On the other hand,  $C_0$  is composed of  $w$ , together with all end-unlinked diagrams that have no articulation points. The latter are built by inserting  $\Lambda$ 's between the termini of any internal  $f$  links, and so

$$C_0 = w + \text{diagram with two nodes and a wavy line} + \text{diagram with three nodes and wavy lines} + \dots \quad (17)$$

But (16) can be written as

$$e * C_1 = f * \Lambda, \quad (18)$$

where  $e = 1 + f$ , leading us to the second relation between  $\Lambda$  and  $C$ :

$$e * C = e * w + \text{diagram with two nodes and a wavy line} + e * \text{diagram with three nodes and wavy lines} + \dots \quad (19)$$

to accompany (14), now written as

$$\Lambda - C = C \zeta \Lambda \quad (20)$$

## 4 Mapping onto Fluids

The practical theory of classical simple fluids in thermal equilibrium has had a long period of development, entailing a sequence of more and more

sophisticated approaches [4]. For uniform simple fluids not at thermodynamic singularities and not with long range forces, little remains to be done. And the non-uniform situation is increasingly under control. Let us indicate that we are speaking of a fluid - initially related to the homopolymer under study only by having a common pair interaction,  $v_L(r, r') = v(r, r')$  - by appending a subscript ( $L$ ). For present purposes, it's sufficient to observe that almost all of the older approximations posit an algebraic relationship (or functional relation in more recent versions) between the dimensionless pair correlation function

$$h_L(r, r') = \frac{n_L(r, r')}{n_L(r)n_L(r')} - 1 \quad (21)$$

and the direct correlation function  $c_L(r, r')$ , directly related to the external potential - density linear response.

In classical thermal equilibrium,  $h_L$  and  $c_L$  satisfy identically the Ornstein-Zernike equation [5], written in continuous matrix form as

$$h_L - c_L = c_L n_L h_L, \quad (22)$$

where  $n_L$  is the particle density as diagonal operator  $\langle r | n_L | r' \rangle = n_L(r) \delta(r - r')$ . We then need a second relation or closure to obtain both  $h_L$  and  $c_L$ . One of the most effective reasonable approximations for short-range forces is the P.Y. relation [6], which in terms of Boltzmann factor  $e$  and Mayer function  $f = e - 1$  of the pair interaction  $v$  reads

$$e * c_L = f * h_L + f, \quad (23)$$

where again the  $(*)$  denotes element by element multiplication.

Comparison between the pair (22,23) and the pair (20,19), is suggestive. If we terminate (19) at first order:

$$e * C = f * \Lambda + e * w, \quad (24)$$

becomes identical with (22) under the assumption

$$C = K c_L, \quad \Lambda = K h_L, \quad \zeta = n_L / K \quad (25)$$

if the condition, for any fixed constant  $K$ ,

$$K f = e + w \quad (26)$$



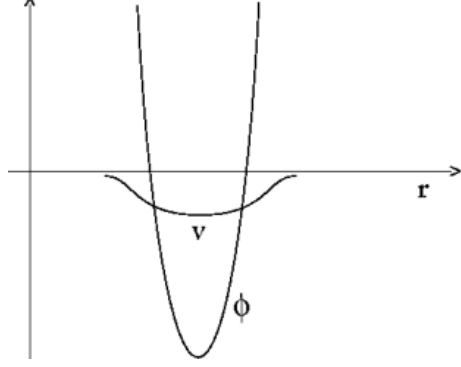


Figure 3: Example of eq.(27)

is satisfied - and (20) and (23) are identical as well. Expressed in terms of the general pair interaction  $v$  and the next neighbor potential  $\phi$ , eq. (26) says that

$$e^{\beta v} + \frac{1}{K} e^{-\beta \phi} = 1 \quad (27)$$

is satisfied. For example, it is sufficient to choose  $v$  as, qualitatively, a reduced version of the highly attractive localized  $\phi$ . Note that according to our correspondence,  $n_L = K\zeta$  may appear as a quite high density in its confined domain. Clearly,  $(1/\beta) \ln K + \phi > 0$  is required by (27).

Once we have used the P.Y. approximation to produce a fluid corresponding to the homopolymer under consideration, we can, in a logically tenuous fashion, analyze the fluid by any other convenient approximation method. Whatever approximation is used, the derived end result is the expression of the polymeric monomer density resulting from the imposed containment potential represented by  $\zeta(r)$ . It's only necessary to translate this into equivalent fluid language. From (6), (13) and (25), we have at once  $\Xi^{(p)} = \langle 1 | \zeta + \zeta \Lambda \zeta | 1 \rangle = \frac{1}{K} \langle 1 | n_L + n_L h_L n_L | 1 \rangle$ , or

$$\Xi^{(p)} = \frac{\langle 1 | S_L | 1 \rangle}{K}, \quad (28)$$

where  $S_L(r, r') = n_L(r, r') - n_L(r)n_L(r') + n_L(r)\delta(r - r')$  is the complete Ursell function or generalized structure factor of the fluid, also appearing as the density-density correlation function.

## 5 Discussion

The picture of an equivalent non-chain fluid is a bit deceptive. At first glance, it resembles the familiar statistical model of biopolymers, itself an offshot of the Lifschitz homopolymer condensation transition model [7]. But the difference is seen most vividly in a situation in which there is an unconstrained volume - constant external potential - bounded by a hard wall container. The “dual” fluid to the polymer would then have a constant density, terminated by zero density at the boundary, and an internal potential structured to produce the required uniform fluid. Some meaningful conclusions can be arrived at in this situation without an in-depth analysis.

Suppose we restrict attention to observations at the correlation length scale of resolution. On this scale, one knows that, clearly,

$$\begin{aligned} S_L(r, r') &= S_L(r - r'; n_L(r)) \\ &= \delta(r - r') \int S_L(R; n_L(r)) dR \end{aligned} \quad (29)$$

where  $S_L(R; n_L)$  is the density-density correlation for a uniform system of density  $n_L$ . Since

$$\int S_L(R; n_L) dR = \frac{\delta n_L}{\delta \beta \mu_L}, \quad (30)$$

this implies that

$$\int \int S_L(r, r') dr dr' = \int \frac{\delta n_L(r)}{\delta \beta \mu_L(r)} dr, \quad (31)$$

and consequently that

$$\begin{aligned} n(r) &= \zeta(r) \frac{\delta}{\delta \zeta(r)} \ln \Xi^{(p)}[\zeta] \\ &= n_L(r) \frac{\delta}{\delta n_L(r)} \frac{\delta n_L(r)}{\delta \beta \mu_L(r)} / \int \frac{\delta n_L(r')}{\delta \beta \mu(r')} dr', \end{aligned} \quad (32)$$

all of which is at  $n_L(r) = K\zeta_0$ . This would seem to indicate that the floppy chain, on averaging over all configurations, would simply fill available space uniformly (since  $n_L(r)$  has no spatial dependence). But this is only true if the correlation length is much smaller than the diameter of the confining volume. For example, in the primitive Van der Waals mean field model [8], in which

$$\ln n_L(r) = \beta \mu_L(r) + \frac{1}{2} \int n_L(r) n_L(r') \left( e^{-\beta v(r, r') - 1} \right) dr', \quad (33)$$

it is easy to see that (32) for a uniform fluid would read

$$n = \frac{1}{V} \left( \frac{1 - 2n_L^2 B}{1 + 2n_L^2 B} \right), \quad (34)$$

where  $B$  is the second virial coefficient, negative for attractive  $v$ , and  $V$  the confinement volume. Then, the needed divergence of  $nV$  for large  $V$  at "resonant"  $n$ , would imply a divergent correlation length, and so in an exact solution, the density would rise only gradually from its surface to bulk value, compatible with a confined polymer transported throughout the volume.

One can of course also go beyond the equivalent fluid picture, but certainly the domain untouched in our treatment is that of heteropolymers. Statistical models are readily constructed by including species dependences in the one and two-body potentials, but the statistical distribution is broad unless the units are at least taken as short subsequences of monomers, thereby introducing multiple internal degrees of freedom. This strategy is being investigated, and in fact was implemented at a very crude level some time ago in the context of including bond angle and dihedral angle restrictions to accord with reality even in heteropolymers [3].

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